Argonne Pational Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

Part IV. The Fluid Bed Fluorination of $\rm U_3O_8$

by

R. L. Jarry, A. V. Hariharan, G. Manevy,J. Fischer, J. J. Stockbar, J. G. Riha,T. D. Baker, and G. W. Redding

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ANL-6763
Chemical Separations Processes for Plutonium and Uranium (TID-4500, 24th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY 9700 South Cass Avenue Argonne, Illinois 60440

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

PART IV. THE FLUID BED FLUORINATION OF U308

by

R. L. Jarry, A. V. Hariharan, G. Manevy, J. Fischer, J. J. Stockbar, J. G. Riha, T. D. Baker, and G. W. Redding

Chemical Engineering Division

October 1963

Part I of this series is ANL-6742 Part II of this series is ANL-6753 Part III of this series is ANL-6762

Operated by The University of Chicago under Contract W-31-109-eng-38 with the U. S. Atomic Energy Commission

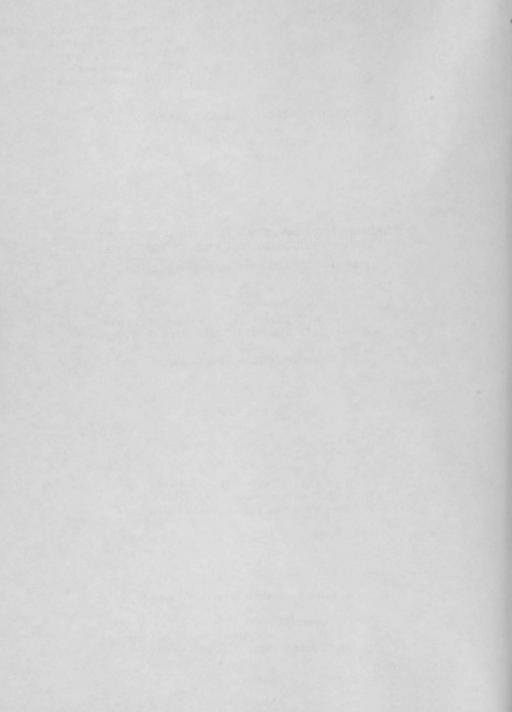


TABLE OF CONTENTS

		Page
ABST	RACT	3
I.	INTRODUCTION	4
II.	EXPERIMENTAL	5
	1. Materials	5
	2. Apparatus	5
	3. Procedure	7
III.	RESULTS AND DISCUSSION	9
IV.	APPENDIX A - Oxidative Decladding of Stainless Steel-clad and Zircaloy-clad Uranium Dioxide Pellets.	13
v.	APPENDIX B - The Kinetics of the Fluorination of Uranosic Oxide	16
VI.	SUMMARY	21
VII.	ACKNOWLEDGMENT	22
VIII.	BIBLIOGRAPHY	23

LIST OF FIGURES

No.	<u>Title</u>	Page
1.	Fluid Bed Fluorination Reactor	6
2.	Gas-Solids Distributor for $l\frac{1}{2}$ -in, Fluidized-bed Reactor	6
3.	Powder Feeder for Fluidized-bed Reactor	7
4.	Photograph Showing Type 304 Stainless Steel-clad Uranium Dioxide Fuel Elements after Various Stages of Oxidation	15
5.	Fluorination of U_3O_8	18
6.	Variation in Reaction Rate Constant, k' (min $^{-1}$), with Temperature for the Fluorination of $U_3O_8\ldots\ldots$	19
	LIST OF TABLES	
No.	Title	Page
1.	Experimental Conditions Affecting Elutriation of U_3O_8 from a Fluidized Bed during Fluorination	9
2.	Effect of Temperature on the Fluid-bed Fluorination of $\ensuremath{U_3O_8}$.	10
3.	Fluid-bed Fluorination of U_3O_8	11
4.	Oxidative Decladding of UO ₂ Pellets Clad in Type 304 Stainless Steel or Zircaloy	14

**Variation in Resction of Upon Testson

**Provider Fooder for Fluidized and Resulton

**Provider Fooder for Fluidized and Resulton

**Provider Fund Showing Pype 10: Statistics Steel-cital Ursaling

**Provider Fund Elements after Various Stages of Outcotton

**Provider of Upon

**Provider in Resction Rate Constant & (min*), with Tests

**Presented to Find Fluidized Constant of Upon

**Provider of Conditions Associate Statistics of Upon

**Provider of Temperature on Upon

**Provider Outcompanion of Upon

**Provider of Temperature on Upon Fluid-bed Fluorination of Upon

**Provider Outcompanion of Upon

**Provider Outcompanion of Upon

**Provider Outcompanion of Upon

**Provider Outcompanion of Upon

**Provider Fluorination of Upon

**Provider Outcompanion of Upon

**Pro

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

Part IV. The Fluid Bed Fluorination of U3O8

by

R. L. Jarry, A. V. Hariharan,* G. Manevy,** J. Fischer, J. J. Stockbar, J. G. Riha, T. D. Baker, and G. W. Redding

ABSTRACT

In one of the processes under development, the uranium and plutonium content of a spent reactor fuel of the Dresden type would be fluorinated in a fluid-bed reactor to produce the volatile uranium and plutonium hexafluorides. The study of the fluorination of U_3O_8 was undertaken because it is the major product obtained in an oxidative decladding step that is being proposed for the removal of uranium and plutonium from stainless steel-clad and Zircaloy-clad fuel elements. The study will also provide data needed for the development of apparatus and procedures for future work with mixtures of uranosic oxide and plutonium dioxide.

Experiments were performed to determine the optimum reaction conditions for the conversion of U_3O_8 to uranium hexafluoride and for minimizing the elutriation of unreacted U_3O_8 from the fluid bed. Elutriation of U_3O_8 from the fluid bed was minimized when a fluid bed height of 8 in. of 120 mesh alumina, a fluorinating gas phase containing 20 v/o fluorine, and a reaction temperature of 500 C were employed. Conversion of greater than 99 percent of the U_3O_8 to uranium hexafluoride was obtained when the feeding-fluorination period, in which the U_3O_8 powder was fed into the fluid bed and the major part of the fluorination was accomplished by reacting the oxide with 20 v/o fluorine, was followed by a recycle-fluorination period of 5 hr at 500 C with 100 percent fluorine.

Kinetic data for the fluorination of U_3O_8 , obtained by means of a thermobalance, are reported for the temperature range from 300 to 400 C. The data were treated by the diminishing-sphere model. Experimental results are also presented for the oxidative decladding of stainless steel-clad and Zircaloy-clad uranium dioxide pellets.

^{*}Affiliate, Institute of Nuclear Science and Engineering.

^{**}Appointee, from Atomic Energy Commission, France.

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID LED PLUICKING VOLATILITY PROCESSES

Part IVI The Build Bed Flubrination of U.O.

V.

R. J. Stockborg J. W. Brilberom. C. Manevy. ** J. Fischer:

ABSTRAGT

In one of the progresses under development, the uranium and plutionium content of a spent reactor had of the Dresden type would be fluorished in a fluid-bed reactor to produce the volatile uraniom and plutonium installation of U.O. was independent beautiful of the the study of the fluorished in an oxidative decladding step that its beautiful proposed for the removal of uranium and plutonium from stanlesses the teacher that the removal of uranium and plutonium from stanlesses are elected for the usvelopment of spentates and procedures for himse data peaced for the usvelopment of apprentix and procedures for himse with mixtures of uranosic oxide and platenium dioxide.

Experiment were postermed to determine the optimize reaction conditions for the conversion/O₂ is presume herafly pride and for mine this obstantion of nurse feed U₃O₃ from the fluid bed. Fluttlates of U₂O₃ from the fluid bed. Fluttlates of U₃O₄ from the fluid bed retailed at a substantial U₃O₄ from the fluid bed retailed at a substantial U₃O₄ from the fluid bed retailed to the fluid the U₃O₅ from the fluid contained when the U₃O₅ for the fluid the fluid

Historic data for the Americation of W.O. obtained by means of a theorem the land start reported for the temperature range from 800 to 400 C. The data were freeled by the simulational sphere model. Experimental regular are also presented for the oxidative decladding of stainless steel-cladding of stainless steel-cladding of stainless steel-cladding of stainless.

^{*} Aufitiate. discitute of Nuclear Science and Engineering

I. INTRODUCTION

In the conceptual flowsheet of a fluid-bed fluoride volatility process, $^{(1)}$ the uranium and plutonium content of spent oxide fuels will be recovered by fluorination to produce the volatile hexafluorides of uranium and plutonium. The process will employ a fluid-bed reactor as the fluorination vessel and will use alumina as the fluidized medium. One of the schemes that is being considered for the decladding of the spent fuel employs an oxidation step to separate the uranium dioxide and plutonium dioxide from the stainless steel cladding or Zircaloy cladding as a mixture of $\rm U_3O_8$ and plutonium dioxide. The oxide mixture produced by this oxidation process is a finely divided, free-flowing powder. This was shown in experiments performed to test the efficacy of the oxidative decladding technique (see Appendix A).

Two alternative schemes have been proposed for carrying out the combination of oxidation and fluorination reactions. In one, the oxidation and fluorination steps would be performed in the same fluid-bed reactor. The oxidation of the spent oxide fuel would be performed in the lower section (oxidation zone) of the fluid bed. The $\rm U_3O_8$ fines formed in the oxidation zone would be transported to the upper section (fluorination zone) of the fluid-bed reactor by the oxidizing gas stream. In the fluorination zone, the oxide fines are fluorinated by means of fluorine which is introduced into the reactor at a point just above the oxidation zone. The second scheme would employ a separate oxidation reactor and the oxide powder formed would be fed into the fluid bed of the fluorination reactor by gas transport in a nitrogen stream used to fluidize the bed.

In previous laboratory work on process development, removal of plutonium from mixtures of alumina, uranium dioxide, plutonium dioxide, and fission product element oxides by fluorination at 450 to 550 C had been studied. These studies, which were described in the first report in this series, (2) indicated that plutonium removal from the Alundum bed could be increased by oxidizing mixtures containing uranium dioxideplutonium dioxide solid solutions to $\rm U_3O_8$ -plutonium dioxide mixtures before fluorinating the mixtures.

In the experimental work described herein, the second reaction scheme, in which the uranium dioxide was first oxidized in a separate vessel and then fed into the fluid-bed fluorinator, was used. A prototype fluid-bed fluorinator was set up for use with uranium alone in order to test and develop apparatus and procedures for subsequent work with plutonium dioxide-U₃O₈ mixtures. Fluorination experiments were performed to determine the optimum conditions of temperature, U₃O₈ powder feed rate, and reaction time for conversion of the U₃O₈ to uranium hexafluoride. Ancillary experimental work was performed on the oxidative removal of uranium dioxide pellets from stainless steel and Zircaloy cladding (see Appendix A) and on the kinetics of the reaction between U₃O₈ and fluorine (see Appendix B).

In the conceptian flowsheed of a find-bed sheet deviatility procuperson which are distincted to produce the volatile excitionates of orderior
covered by fluorination to produce the volatile excitionations of orderior
covered by fluorination to process will employ a fluid-bed reactor as the fluoricovered process will use alumina as the fluid-bed reactor as the fluoricovered and will use alumina as the fluid-bed reactor as the fluoricovered and will use alumina as the fluid-bed reactor as the fluoricovered to being considered for the deciding of the spent fluid inside from
the statistics are of cividing of first ordered by this oxidation process to
pluiding directions of the conde mixture produced by this oxidation process to
a finally divided free-flowing powders. This was shown to experiments particular
formed to test the efficiency of the oxidative decisading featurings free
Appendix A).

I would be led at a point by the excitation and the street compared to the content of the conten

in previous laboratory work on process development, removal of plutonium from mixtures of alumina, around discident plutonium discident and fission product element, oxides by illustration at 170 to 550 C had been studied. These liquides which were described in the first report in this series (2) and that plutonium removal from the Alumdum bed could be increased by oxidizing mixtures containing araptum discident plutonium discident plutonium discident plutonium discident plutonium discident plutonium discident mixtures before plutonium discident mixtures before fluorinating the mixtures.

in the experimental work described agree at the second reaction scheme, to which the transmire dioxide was first exidized in a separate vesse and then find into the thuist-bed fluorimator, was used. A prototype fluid bed fluorimator was set up for use with uramum stone in order to test and develop or an interest of the prototype of the companies of the companies of the prototype of the conditions of temperature, U.O. powder feed rate, and reaction time for conversion of the U.O. to a namum hexaltuoride. Ancillary experimental work was performed on the examinant hexaltuoride. Ancillary experimental work was performed on the examinant flowing (see Appendix A) and on the measure of the reaction between U.O. and illuorine (see Appendix A) and on the measure of the reaction between U.O. and illuorine (see Appendix A).

II. EXPERIMENTAL

1. Materials

The $\rm U_3O_8$ used in this work, obtained from Union Carbide Nuclear Company, had a surface area of 0.74 sq m/g, as measured by nitrogen adsorption, and an average particle diameter of 3.1 μ . Chemical analysis of the $\rm U_3O_8$ indicated a uranium content of 84.46 percent (theoretical content: 84.80 percent). Spectrochemical analysis indicated that the principal contaminants of the oxide, expressed in ppm, were: Al, 30; Cr, 10; Fe, 50; Mo, 30; Ni, 50; and Si, 30. Commercial-grade fluorine, which was passed through a sodium fluoride trap at 100 C to remove hydrogen fluoride, was used. The nitrogen, which was used as the fluidizing gas and also as a diluent for the fluorine, was passed through a trap containing molecular sieves to remove water. High-purity fused alumina was employed as the inert fluidized material.

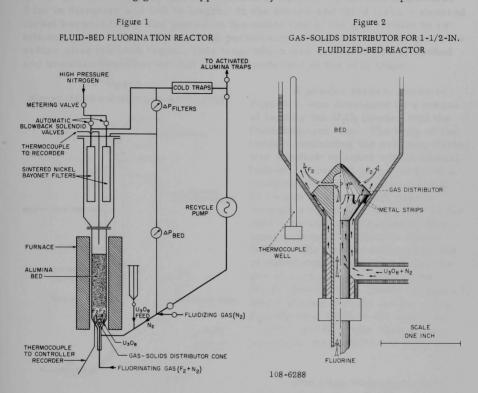
2. Apparatus

The fluorination apparatus consisted of the following major components: (1) a $1\frac{1}{2}$ -in.-diameter fluid-bed fluorinator; (2) a powder feeder; (3) a system of cold traps to condense uranium hexafluoride; (4) a Lapp diaphragm pump employing a remote head to circulate the gas phase; (5) activated alumina traps for the disposal of fluorine; and (6) manifolds supplying fluorine, nitrogen, and vacuum service.

Figure 1 is a schematic representation of the fluid-bed fluorination reactor. The lower section, which contained the alumina bed, was fabricated from a 1-ft section of $1\frac{1}{2}$ -in.-diameter, schedule 40 nickel pipe. The upper section of the reactor, the disengaging chamber, was fabricated from a 1-ft section of 3-in.-diameter, schedule 40 nickel pipe, and contained two sintered nickel bayonet filters through which the reactor off-gases passed. A gas and solids distributor was located within the conical bottom of the lower reactor section. This device insured a uniform distribution of the uranosic oxide powder in the fluid bed and provided an inlet for the fluorine-nitrogen mixture into the fluid bed above the entry point of the oxide powder.

Tests showed that satisfactory fluidization of the solids and distribution of the gas were accomplished when the fluidizing gas and $\rm U_3O_8$ entered the bed through an annular inlet, approximately half the diameter of the reactor. The annulus was provided between the conical bottom of the reactor and the double-cone gas-solids distributor, as shown in Figure 2. Small metal spacers, attached to the bottom of the gas-solids distributor, were interposed between the distributor and the conical bottom of the reactor. Fluorine entered the distributor by means of a central tube connected to the bottom of the distributor, and the gas then entered the bed through eight holes located in the upper portion of the distributor. Twenty grams of

powder, having an average particle diameter of 6μ , could be fed in 1 min into a 5-in.-high alumina bed composed of 60 mesh particles. The flow rate of the fluidizing gas was approximately 0.5 cfm at room temperature.



The reactor was heated by a resistance furnace which had three heating elements. The two lower elements were controlled by a thermocouple inside the reactor at the level of the fluorine inlet, whereas the upper element was controlled by a thermocouple placed at about the middle of the outside surface of the reactor.

An automatic blowback system, described by Loeding $\underline{\text{et}} \ \underline{\text{al.}}, (3)$ was employed to return solids which reached and were retained on the surface of the sintered nickel filters. A Venturi throat and jet were used in this system to deliver a high-speed flow of nitrogen through the bayonet filter countercurrently to the normal gas flow of the system. Since the blowback procedure was alternated between the two filters, no interference with the normal flow of the reaction gases resulted.

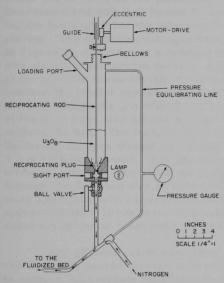
The of the fluidizing was approximately 0.5 cfm at room temperature.

the reactor was noticed by a resistance brushe which had three or heating elements. The two-lower elements were controlled by a thermode couple inside the reactor at the two-lower blue the function inlets whereas the upper element was controlled by a thermosouple placed at about the middle of the outside auriace of the reactor.

"At setomate blowback system; described by Localing St al T T was completed to meturn solids which reaches and were retained on the surface of the sintered nickel litters. A Vangurd throat and jet were used in this system to deliver a high-speed flow of hirrogen through the bayonet (iff or compressive eaching to the normal gas flow of the system. Sints the blowback proceedure was alternated between the two filters, no futeric rence with the normal flow of the reaction gases resulted.

The cold-trap system used to condense the uranium hexafluoride consisted of three traps in series. The traps were refrigerated at about -80 C by use of a carbon dioxide-trichloroethylene slush. The traps were 4 in. in diameter and 1 ft in length. In the second and third traps a sintered nickel bayonet filter was placed on the outlet line of the gas stream to retain any particulate matter. Atrap packed with sodium fluoride was placed in series after the cold traps. This trap, which was heated to 100 C, sorbed any uranium hexafluoride that had not condensed in the cold traps.

Figure 3
POWDER FEEDER FOR FLUIDIZED-BED REACTOR



108-6287

A powder feeder, shown in Figure 3, was developed as a means of feeding the U₃O₈ powder into the fluidizing-gas line. The body of the feeder, containing the uranosic oxide, was a hollow cylinder with a conical bottom. A conical plug was given a reciprocating up-and-down motion by means of a rod which passed through a bellows on the cover of the container and was attached to an eccentric shaft of a variable-speed motor. The powder released by the reciprocating plug dropped into the gas stream and was injected into the fluidized bed as shown in Figure 1. Tests showed that the feeder could provide feed rates in the range between 2 and 20 g/min when the diameter of the particles of U3O8 was 6 M.

The Lapp diaphragm pump, used to recirculate the fluorine, had a rated flow capacity of 0.5 cfm at a

discharge pressure of 15 psig and atmospheric pressure intake. The remote head of the pump is constructed of Monel and nickel on the gas pumping side, and the impulse is transmitted from the compression head by means of a transmission line filled with fluorolube oil. Measurements of flow rate were made by means of a thermal flowmeter of the type described by R. Kessie. (4) Flow calibration of the pump-flowmeter combination was accomplished with nitrogen using a wet test meter.

3. Procedure

The fluorinations of U_3O_8 were performed in two reaction periods. In the first period, which will be referred to as the feeding-fluorination period, the U_3O_8 powder was injected into the fluid bed, and the major part

of the oxide was converted to uranium hexafluoride by means of a gas mixture of 20~v/o fluorine in nitrogen. In the second period, which will be referred to as the recycle-fluorination period, the fluorine content was raised to about 100~percent, and the gas recycled through the Lapp pump and back to the fluidized bed. The last traces of uranium were removed during the recycle-fluorination period. In future experiments with uranium dioxide-plutonium dioxide solid solutions, this step will serve to remove the plutonium from the bed material.

The general operating procedure for the fluorinations was as follows: About 400 to 500 g of 120 mesh fused alumina was placed in the fluid bed fluorinator and was then heated to the operating temperature of 500 C. During the heating period the nitrogen flow needed to fluidize the bed was started. The fluidizing nitrogen entered the bottom of the reactor as shown in Figure 1. A charge of a mixture of U₃O₈ and alumina in a 2:1 weight ratio was placed in the powder feeder. Alumina was mixed with the U3O8 to improve the flow characteristics of the oxide powder. When the reactor reached the proper operating temperature the fluorine flow was started into the bed through the gas distributor cone. The fluorine, which was 20 v/o of the total flow, was diluted with an equal quantity of nitrogen before it entered the bed. The U₃O₈ alumina mixture was then introduced into the fluidizing nitrogen stream and thence into the fluid bed at a rate of about 3 g of U_3O_8 per minute. The gas velocity in the $\frac{3}{9}$ -in.-diameter fluidizing nitrogen inlet line into which the U₃O₈ is fed was 5 ft/sec. Total flow rate through the fluid bed was 12 liters/min, with the fluidizing nitrogen contributing approximately 7 liters/min, and the mixture of fluorine and nitrogen approximately 5 liters/min. The superficial velocity in the fluid bed was about 0.6 ft/sec at room temperature.

The effluent gas stream from the fluorinator, when the gas is not recirculated, passed through cold traps and a sodium fluoride trap in order to remove the uranium hexafluoride, and then through an activated alumina trap which reacts with and removes excess fluorine. The effluent was then exhausted to the atmosphere. This once-through flow was continued while the $\rm U_3O_8$ -alumina mixture was being fed into the fluid bed. In the cases in which no recycle was used, the once-through flow was continued for $\frac{1}{2}$ hr after the feeding was completed.

Following the feeding-fluorination period, the fluorine content of the gas phase was brought to approximately 100 percent and the recycle period was started. The recycle flow was carried out for a period of 5 hr. After the reaction period had been completed, the sodium fluoride trap and the cold traps, which were maintained at -78 C, were evacuated to remove the residual gas phase. The traps were then warmed to room temperature and weighed to assay the amount of uranium hexafluoride collected. The fluid-bed alumina was removed from the reactor and sampled for uranium analysis. The small amount of mixture of U₃O₈ and alumina which was retained in the disengaging section was removed and submitted for uranium analysis.

III. RESULTS AND DISCUSSION

In the first series of experiments, the parameters affecting the elutriation of U_3O_8 from the alumina bed were explored. The elutriation of U_3O_8 from the alumina bed results in the deposition of solids containing uranium on the surfaces of the disengaging chamber and filters, where no fluorination of the U_3O_8 occurs. For these experiments, the bayonet filters were removed from the disengaging chamber, and the solids which passed through the disengaging chamber were trapped in a filter that was placed in a separate outside chamber of the reactor. By weighing the filter before and after the experiment, the quantity of unreacted U_3O_8 and alumina elutriated from the fluid bed could be determined. A determination of the quantity of U_3O_8 elutriated was made by dissolving the U_3O_8 in the elutriated solids with nitric acid. The residual alumina was then dried and weighed, the weight of U_3O_8 being obtained by differences.

The results obtained in experiments in which the particle size of the alumina, the bed height, and fluorine concentration were varied are shown in Table 1. When the particle size of the alumina was decreased from 60 to 120 mesh, elutriation of U_3O_8 from the bed was reduced from 19.5 to 9.0 percent of the U_3O_8 fed to the bed. When a 50-50 mixture of 60 and 120 mesh alumina was used, the amount of U_3O_8 elutriated was not appreciably less than the amount elutriated when 60 mesh alumina was used.

Table 1

EXPERIMENTAL CONDITIONS AFFECTING ELUTRIATION OF U_1O_8 FROM A FLUIDIZED BED DURING FLUORINATION

Experimental Conditions

Reaction Parameter Varied	Al ₂ O ₃ Particle Size (mesh)	Bed Height (in.)	F ₂ Conc in Gas (v/o)	Percent Elutriation of U ₃ O ₈
Al ₂ O ₃ Mesh Size	120	8	20	9.0
27 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	60	8	20	19.5
	60 + 120a	8	20	19.0
Bed Height	120	4	20	23.0
	120	8	20	9.0
	120	12	20	9.5
Fluorine Concentration	120	8	10	29.0
	120	8	20	9.0
	120	8	30	5.7

aMixture: 50 w/o 60 mesh alumina + 50 w/o 120 mesh alumina.

Variation of the height of the alumina bed also affected the amount of U_3O_8 elutriated from the bed. Increasing the bed height from 4 to 8 in. reduced the amount of U_3O_8 elutriated from 23 to 9 percent of the quantity of U_3O_8 charged to the bed, as shown by the results listed in Table 1. Further increase in bed height, however, did not result in a further reduction in the amount of U_3O_8 elutriated from the bed.

The amount of $\rm U_3O_8$ elutriated from the fluid bed was found to decrease as the concentration of fluorine in the reactant gas was increased. As shown in Table 1, the concentrations of fluorine used were 10, 20, and 30 v/o. With these gas mixtures, the amounts of $\rm U_3O_8$ elutriated were 29, 9.0, and 5.7 percent, respectively, of the amount of $\rm U_3O_8$ originally present. From these data, it is apparent that the elutriation of $\rm U_3O_8$ from the fluid bed will decrease with decreasing particle size of the alumina, increasing bed height, and increasing concentration of fluorine.

In a second series of experiments, the effect of temperature on the fluorination of U₃O₈ to uranium hexafluoride was examined. The bayonet filters were reinserted in the disengaging chamber, and each filter was subjected to a blowback with nitrogen every 5 min during the experiment. As in the earlier experiments, gas recycle was used except during the feeding-fluorination period. Table 2 lists the data obtained for experiments performed at 450, 500, and 550 C. The percentages of U₃O₈ converted to uranium hexafluoride were 92 percent at 450 C, 97.6 percent at 500 C, and 98.5 percent at 550 C.

Table 2

EFFECT OF TEMPERATURE ON THE FLUID-BED FLUORINATION OF $\rm U_{3}O_{8}$

Experimental Conditions

step completed.

Fluid-bed Alumina: 470 g (120 mesh) Feed Material: 100 g U_3O_8 (325 mesh), 50 g Al_2O_3 (120 mesh) Total Gas Flow Rate ($F_2 + N_2$): 12 liters/min at 25 C Superficial Fluidizing Gas Velocity: 1.6 ft/sec at 500 C Gas Velocity in $\frac{3}{8}$ -in.-dia Feed Line: 5 ft/sec at 25 C Filters alternately blown back every 5 min.

Fluorination continued for $\frac{1}{2}$ hr after feeding-fluorination

U_3O_8 Feed Rate (g/min)	Bed Temperature (C)	% Conversion of U_3O_8 to UF ₆ Based on UF ₆ Collected			
2.4	450	92.0			
3.6	500	97.6			
2.4	550	98.5			

Viriation of the height of the olumins bed also affected the amount of U/Os clutriated from the bed. Increasing the bed keight from 4 to 8 in. reduced the amount of U₂O₅ elutriated in om 23 to 9 percent of the quantity of U₂O₅ clarges to the bed, as shown by the results fisted in Table 1. Further increase in bed height however, did not result in a further reduction in the amount of U₂O₅ elutriated from the bed.

The amount of U₃O, similated from the fluid bed was found to decrease, as the concentration of fluorine in the reactant gas was increased. As set we in Table 1, the concentrations of fluorine used were 10, 20, and 30 v/o. With these gas mixtures, the amounts of U₃O₂ effictions were 29, 9.6, and 5.7 percent, respectively, of the amount of U₃O₂ originally present. From these data, it is apparent that the clutrication of U₃O₂ from the fluid bed will decrease with decreasing particle size of the alumina, increasing bed height, and increasing concentration of fluorine.

In a second sories of experiments, the effect of temperature on the fluorination of U₂O₂ to transam hexast soride was examined. The payonet dilters were reinverted in the disengaging chamber, and each filter was a subjected to a blowback with natrogen every 5 mar during the experiments. As in the earlier experiments, gas recycle was used except during the freeding-fluorination portiod. Table 2 lists the data obtained for experiments parformed at 150, 500 and 550 C. The percentages of U₂O₂ converted to transium hexafluoride were 22 percent at 450 C, 57.6 percent at 500 C. and 98.5 percent at 550 C.

I able 2

EFFECT OF TEMPERATURE ON THE FLUID-BED FLOOR U.O.

Experimental Conditions

Fluid-bed Alumina

470 g (120 mesh) 100 g U₂O₃ (325 mesh), 50 g Al₂O₃ (120 mesh) 12 litera/min at 25 C

Total Gas Flow Rate (Fj + N₂):

Superficial Fluidizing Gas Velocity:

Gas Velocity in $\frac{3}{2}$ -in-dia Feed Line: 5 ft/sec at 25 C Filters alternately blown back every 5 min.

Filters alternately blown back every 5 min.

Fluorination continued for $\frac{1}{2}$ by after seeding-fluorination atep completed.

A final series of experiments was performed at 500 C in which a 5-hr recycle period with 100 percent fluorine and an automatic blowback system were employed. During the recycle period, the portion of the feed line immediately adjacent to the reactor was heated to 450 C to facilitate the fluorination of any $\rm U_3O_8$ which might have remained in this area. The experimental conditions used and the results obtained in these experiments are listed in Table 3. The data show that 99 percent or more of the $\rm U_3O_8$ can be converted to uranium hexafluoride by means of a fluid-bed fluorination under the reaction conditions used in these experiments. In one experiment, the 5-hr cycle period was performed at a temperature of 550 C;

Table 3
FLUID-BED FLUORINATION OF U₃O₈

Experimental Conditions	
Fluid-bed Alumina:	120 mesh, 420 g
Uranosic Oxide-Al ₂ O ₃ Feed Mixture:	300 g U ₃ O ₈ ; 150 g Al ₂ O ₃
Feeding-Fluorination Period:	
Bed Temperature:	500 C
Total Gas Flow Rate (at 25 C):	12 liters/min
Fluidizing N2	7 liters/min
Fluorine	2.5 liters/min

Fluorine 2.5 liters/min N₂ in Fluorine 2.5 liters/min Superficial Fluidizing Gas Velocity: 1.6 ft/sec at 500 C Gas Velocity in $\frac{3}{8}$ -in.-dia Feed Line: 5 ft/sec at 25 C

Recycle Period:

Bed Temperature:

Total Gas Flow Rate:

Fluorine Conc in Gas Phase:
Recycle Time:

Temperature of Feed Line:

450 C

		Analytical	Results			
	F ₂ Conc in	Total	U in	% U ₃ O ₈ Conver Based		
U ₃ O ₈ Feed Rate (g/min)	Gas Phase during Recycle (v/o)	Residual U (g)	Al ₂ O ₃ Bed (g)	U₃O ₈ Residue ^a Unreacted	UF ₆	Material ^b Balance (%)
3.7	100	0.26	0.12	99.7	99.8	100.1
3.7	100	0.37	0.24	99.9	98.9	99.0
2.5	100	0.77	0.09	99.8	99.0	99.2
3.5	100	2.28	0.26	99.5	98.5	99.0
5.1c	100	0.13	0.07	100	101	101
4.1	100	0.63	0.24	99.8	97.6	97.8
4.6	100	0.82	0.09	99.7	100	100.3
6.0	100	0.99	0.30	99.6	99.5	99.9
5.9	50	0.57	0.39	99.7	99.2	99.5
3.8	50	0.60	0.11	99.7	99.1	99.4

^aMaterial retained in disengaging chamber and representative sample of bed material analyzed for uranium content, and the total uranium content from both of these sources used to calculate the percent conversion.

bMaterial Balance % = % converted (UF₆ base) + [100 - % converted (Anal base)].

^cBed temperature during recycle fluorination period; 550 C.

parameter remained in disengaging photogram and representative sample of our majoral analysis of provided and the first assented estated assented estated assented assented assented assented as the content of the cont

Animala Dalance A. * A converted (OF, blace) = [100 - M considered (Anal. Secondary) and proceedings of the Constitution of th

at this temperature essentially complete conversion of the U_3O_8 to uranium hexafluoride was achieved. In two experiments the gas phase during the recycle-fluorination period contained 50 v/o fluorine. The conversion obtained in these experiments was essentially the same as that achieved in experiments with 100 percent fluorine.

The higher values of conversion listed under Column 5 in Table 3 are based on the results of analyses for uranium of representative samples of the bed material and the material deposited in the disengaging chamber. Uranium retention in the alumina beds ranged from 0.02 to 0.05 w/o, corresponding to 0.1 to 0.3 g of uranium for total weights of the recovered alumina beds of from 518 to 572 g. The disengaging chamber samples, which ranged in weight from 1 to 3 g, contained from 0.1 to 1.0 g of uranium. The total uranium contents of the alumina beds and disengaging chamber samples represented 0.1 to 0.5 percent of the uranium fed to the reactor. The material balance figures were calculated from the percent conversion figures based on uranium hexafluoride collected and the analyses of the bed and disengaging chamber material as follows:

Material Balance $\% = \% (UF_6 \text{ base}) + [100 - \% (Anal base)].$

The somewhat lower conversion figures based on uranium hexafluoride collected are apparently not due to loss of hexafluoride, since the quantities found on the sodium fluoride were well below the tested capacity of the trap. It is probable that the discrepancy is due to weighing inaccuracies.

The results obtained in this work showed that greater than 99 percent of the 100 g of $\rm U_3O_8$ powder fed to a fluid bed under the reaction conditions used in this study can be converted to uranium hexafluoride. The experimental conditions (shown in Table 3) which were developed during the course of this study will serve as the initial reaction conditions for future work in which mixtures of $\rm U_3O_8$ and plutonium dioxide will be fluorinated.

The high conversions to uranium hexafluoride and the small amounts of $\rm U_3O_8$ found in the disengaging chamber of the reactor indicate that the $\rm U_3O_8$ must be reacted in the narrow zone in which the $\rm U_3O_8$ and fluorine mix. That $\rm U_3O_8$ reacts rapidly with fluorine was shown by kinetic experiments performed over the temperature range from 300 to 400 C (see Appendix B). A reaction rate of 0.02 g of $\rm U_3O_8$ per minute at 400 C was obtained. From the extrapolated reaction rate at 500 C, a reaction time for a particle of $\rm U_3O_8$ of 1.7 min was calculated. An estimate made of the residence time of a particle 12μ in diameter in a fluid bed at a superficial gas velocity of 0.67 ft/sec is 24 min. $^{(5)}$ Therefore, the particles should be reacted completely in the bed, and the conversion obtained in this work tend to substantiate this conclusion.

of the temperature assentially complete conversion of the UsO₂ to uranium according to the was place during the security of the was place during the received fluctuation of the conversion obtained an draw during the temperature of the conversion of the conversio

the ligher values of analyses for wearing of regressions to the best and the respite to the best material and the material deposited in the disenseging chamber.

Or the best material and the material deposited in the disenseging chamber.

Or move retention in the alumina dade ranged from 0.00.00 0.05 who corresponding to 0.1 to 0.3 g of uranium for total weights of the recovered alumina beds of trom 5.00 to 5.00 g. The disenseging chamber samples which recal uranium contents of the alumina beds and disenseging chamber samples represented 0.1 to 0.5 percent of the uranium fed to the resetter. The material ball mee figures were calculated from the percent conversion throtal based or uranium next words calledted and the shalves of the bed and disenseging chamber material as follows:

Material Balance W = N (UF, base) + [100 - N (Anal base)]

The somewhat lower conversion figures based on manium licxelluoride collected and apparently not due to lose of hexalluoride, singe the quantities found on the sodium fluoride were well below the teared capacity of the trap It is probable that the discrepancy is due to weighing in quiradies.

The results obtained in this work showed that greater than 99 per tent of the 100 g of U₂O₃ powder fed to a fluid bed under the reaction conditions used in this study can be converted to uranium begalderide. This expectmental conditions (shown in Table 3) which were developed during the course of this study will serve as the ministreaction conditions for fluid work in which mixtures of U₂O₃ and physonium dustide will be fluid fluoriested.

The Mg Conversions to uranium hexallicatide and the small amounts of U.O. frond in the disengaging chamber of the center inducted that the .U.O. frond in the disengaging chamber of the center inducted that the .U.O. reacts rapidly with Bucine was shown by kinetic experiments performed over the temperature range from 300 to 400 C (see Appendix 3). A reaction rate of 0.02 g of U.O. per minute at 400 C was obtained. From the extrapolated reaction rate at 500 C, a reaction time for a particle of .U.O. of 1 7 min was calculated. An estimate made of the residence thise of a particle 12 in diameter in a floid bed at a superficial gas velocity of 0.67 th see is 24 min. (5) Therefore, the particles should be reacted come, plotely in the bed, and the conversion obtained in this work tend to successful this conclusion.

IV. APPENDIX A

Oxidative Decladding of Stainless Steel-clad and Zircaloy-clad Uranium Dioxide Pellets

Removal of uranium dioxide and plutonium dioxide from stainless steel cladding by oxidation of the uranium dioxide to $\rm U_3O_8$ is being considered as a step which would precede fluorination in a fluid-bed fluoride volatility process. Oxidation of uranium dioxide pellets results in an increase in volume and pulverization of the pellets as $\rm U_3O_8$ is formed. The feasibility of the process was demonstrated at Atomics International, $^{(6)}$ where successful decladding of uranium dioxide pellets clad in Type 304 stainless steel was achieved by oxidation at 400 to 500 C with air or oxygen. In these experiments, in which greater than 99 percent of the uranium dioxide was removed from the cladding by oxidation, holes were punched through the cladding at short intervals along the length of the fuel elements. This procedure resulted in the rupture of the cladding during oxidation, thus allowing greater access of the oxidizing gas to the uranium dioxide pellets. The $\rm U_3O_8$ was separated from the cladding by mildly vibrating the assemblies.

In Appendix A, the oxidative decladding of uranium dioxide fuel elements in a fluid-bed reactor is discussed. The oxidative decladding step not only serves to separate uranium and plutonium oxides from the cladding material, but also serves to produce a uniform feed for the fluidized-bed fluorinator. Fluorination of spent uranium dioxide reactor fuel containing cracked and fragmented pellets results in uneven fluorination conditions if the fluorination is not preceded by oxidation. If oxidation does precede fluorination, finely divided $\rm U_3O_8$ powder with an average particle size of 10 μ and surface areas of 0.5-1.0 sq m/g is produced, and the subsequent fluorination proceeds smoothly.

Introduction of the powdered $\rm U_3O_8$ to the fluid bed fluorinator can be achieved by either of two methods. In one procedure, a section of the spent fuel elements is oxidized and declad in the lower section of the fluid-bed reactor, and the $\rm U_3O_8$ and plutonium oxide powders are transported into the upper section of the fluid bed, where they are fluorinated. In an alternative procedure, the oxidized mixture of uranium and plutonium oxides are mechanically fed to the fluid-bed reactor.

Preliminary experiments in a horizontal tube furnace with $\frac{3}{4}$ -in.long fuel sections which contained UO_2 pellets clad in Type 304 stainless steel tubing (wall thickness, 20 mils) showed the following results:

a) Complete conversion of $\rm UO_2$ to $\rm U_3O_8$ occurred in 3 to 4 hr at temperatures between 450 C and 550 C in a flowing stream of air; finely divided, freely flowing oxide powders were produced.

A MUDON'S A VI

seelacts more obtained and placed on a placed on displaced to the problem of the state of the st

In Appendix A, the exidadive declading of minimum distributions elements in a fluid-hold reactor is discussed. The exidative declading alternates in a fluid-hold reactor is discussed. The exidative declading alternate only serves to expend and placentum estimates alternated for the fluid of the fluid of

Introduction of the councied U₂O₂ to the hold sed fluor instances, a section of the perfective, a section of the specific of two melhods. In one proceeding, a section of the specific first processor, and the U₂O₂ and pluronish oxide powders are transaction of the upper section of the third bed, where they are fluorisated in an alternative procedure, the conditied mixture of a salvan and pluronism quadre are mechanically led to the fluid-bed reactor.

Preliminary experiments in a normoulal tube furnace with \(\frac{1}{2}\)-initial form sections which contained UO, pellets clad in Type 304 accions sections:

a) a Complete conversion of UO, to U,O, occurred in 3 to 4 hr at temperatures between 450 C and 550 C in a flowing smeak of alst finely divided, freely flowing oxide pewders were produced.

- b) The oxidized material could easily be removed from the cladding tube by gentle vibration of the fuel elements.
- c) Although oxidation is slightly faster at temperatures of 450 or 550 C in a stream of pure oxygen, the material has a tendency to cake and stick to the cladding.

Further work was carried out in a fluidized bed of alumina with UO2 pellets clad in $5\frac{1}{2}$ -in.-long sections of Type 304 stainless steel or in Zircaloy. Slots $(\frac{1}{8} \text{ in. } \times \frac{1}{32} \text{ in.})$ were milled along the length of the cladding tubes with separations of $\frac{3}{8}$ in. between the ends of the slots. The wall thicknesses of the Type 304 stainless steel were 10 to 20 mils, and the thickness of the Zircaloy cladding was 30 mils. The experiments were performed at 450 C, with dry air as the fluidizing and oxidizing gas. A single run, in which the UO2 pellets were clad in Type 304 stainless steel tubing having a wall thickness of 20 mils, was carried out at 550 C with air as the oxidant. The results of these experiments are given in Table 4. In all cases an initial swelling of the cladding tube was followed by a partial and then complete splitting of the cladding along the slit line. With 10- and 20-mil-thick stainless steel cladding, the tubing split open along its entire length after 2 and 4 hr of oxidation, respectively. Complete removal of the U₃O₈ product was accomplished by oxidizing for an additional 1 or 2 hr. In the experiment at 550 C, 20-mil-thick stainless steel was completely split after 6 hr of oxidation. The different stages of the splitting of the cladding are shown in Figure 4. The cladding shown in Figure 4 was stainless steel with a wall thickness of 20 mils.

Table 4

OXIDATIVE DECLADDING OF UO_2 PELLETS CLAD IN TYPE 304 STAINLESS STEEL OR ZIRCALOY

UO₂ Pellets: NUMEC, size: $\frac{7}{16}$ -in. dia, $\frac{7}{16}$ -in. length Fluid-bed Material: 500 g of 120 mesh Al₂O₃ (Norton Co.) Fluidizing Gas: Air (linear velocity, 0.3 ft/sec at 25 C) Size of Clad Pins: $5\frac{1}{2}$ -in. long, with $\frac{1}{8}$ -in. $x\frac{1}{32}$ -in. slots milled along the length with a $\frac{3}{8}$ -in. spacing between ends of slots. Number of Pellets: 12; total wt UO₂, ~120 g.

	Type and Wall	Percent Retention ^a of UO_2 in Cladding with Time (hr)							Average Rate	
Temperature (C)	Thickness of Cladding (mils)	1	2	3	4	5	6		8	of Removal (g/hr) ^b
450	SS, 10		65.7°	-	0.02	-			-	30d
450	SS, 20	-	93.4	-	18.2¢	0.03	-	-	- 100	24d
450	Zircaloy, 30	-	98.6	-	87.2	-	10.0¢	-	0.15	15d
550	SS, 20	-	91.4	-	91.1	_	10.0°	0.03	-	17e

 a Calculated on basis of initial weight of UO_{2} .

bCalculated using time necessary for complete removal of oxide from cladding.

Clad tube split open completely at the end of this period.

dFine powders of oxidized material in bed.

eSlight caking of material observed.

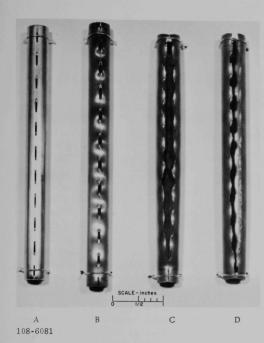


Figure 4
PHOTOGRAPH SHOWING TYPE 304 STAIN-LESS STEEL-CLAD URANIUM DIOXIDE FUEL ELEMENTS AFTER VARIOUS STAGES OF OXIDATION

- A Original Element, 20-mil-thick Type 304 stainless steel cladding.
- B Cladding after 2 hr of oxidation.
- C Cladding after 4 hr of oxidation.
- D Cladding after 5 hr of oxidation.

In Figure 4, \underline{A} is the original element, \underline{B} is a similar specimen after 2 hr of oxidation, \underline{C} is a specimen after 4 hr of oxidation, and \underline{D} is a specimen after 5 hr of oxidation and complete removal of the uranosic oxide powder. Several observations can be made from the results of these experiments:

- Oxidative decladding of uranium dioxide pellets clad in Type 304 stainless steel or Zircaloy is feasible in a fluid bed at 450 C, with air as the oxidant.
- 2) Milling slots along the length of the cladding allows greater access of the oxidizing gas to the pellets, promotes splitting of the cladding along the slot line, and makes easier the removal of $\rm U_3O_8$ from the cladding.
- 3) The time necessary for complete removal of the $\rm U_3O_8$ formed appears to be dependent on the time necessary to achieve complete splitting of the cladding, which in turn appears to be dependent on the thickness of the cladding.



V. APPENDIX B

The Kinetics of the Fluorination of Uranosic Oxide

The oxidative decladding of uranium dioxide fuel elements will produce finely divided, powdered U_3O_8 . In the fluid-bed fluoride volatility process, the U_3O_8 will be fluorinated in a fluid-bed reactor. The U_3O_8 will either be produced in the same fluid bed in which the fluorination will be carried out, or prepared in a separate reaction vessel and injected into the fluid bed of a fluorinator. It is necessary that the U_3O_8 be fluorinated during its residence time in the fluid-bed medium, in order to minimize elutriation of the U_3O_8 powder to cooler portions of the reactor, where reaction would not take place. A study of the kinetics of the reaction of fluorine with U_3O_8 was made in order to obtain information from which the residence time necessary to completely react a particle of U_3O_8 with fluorine in a fluid bed could be calculated.

Two batches of $\rm U_3O_8$ were used in this study. The first, prepared by the New Brunswick Laboratory of the AEC and designated as NB-15, had a certified purity of 99.9+ percent. The second batch, prepared by Union Carbide Nuclear Corporation and designated as UCN, had a uranium content of 84.99 percent (theoretical for $\rm U_3O_8$, 84.80). The surface areas, as measured by nitrogen adsorption of the NB-15 and UCN source materials were 0.14 and 0.28 sq m/g, respectively. The fluorine used was commercial grade from which hydrogen fluoride was removed by passing the gas through a trap filled with sodium fluoride heated to 100 C.

The fluorination experiments were performed with a thermobalance that was specially designed for use with fluorine. The main components of this thermobalance, which has been described in detail by Johnson and Fischer, (7) are a Sartorius Selecta analytical balance, equipped for automatic weight recording, and a vertical, tubular reaction chamber. A nickel sample pan, upon which the U_3O_8 powder was placed, was suspended in the reaction chamber by a Monel chain attached to the stirrup of the Sartorius balance. Fluorine was passed through a preheater before the gas entered the reactor. The flow rate of the fluorine was measured by a thermal flowmeter. A thermocouple positioned directly beneath the sample pan sensed the reaction temperature. The output of the thermocouple was measured with a Rubicon Type B potentiometer. A multipoint recording potentiometer was used to monitor the temperature of the furnace used for preheating the gas, the temperature of the reaction furnace, and the output of the thermal flowmeter.

In a typical experiment, 400 mg of U_3O_8 were placed on a tared nickel pan and then lowered into the reaction chamber which was preheated to the desired temperature. During this stage of the experiment, a flow of nitrogen was maintainted through the reactor. The weight of the oxide sample was checked on the Sartorius balance while temperature equilibrium between gas

The Kinetics of the Fluorination of Uranosic Oxide

The oxidative decladding of uranium dioxide (sel elements will produce finely divided, powdered U₃O₃. In the fluid-bed fluoride volatility process, the C₃O₅ will be fluorinated in a fluid-bed reactor. The U₃O₅ will either be produced in the same fluid bed in which the fluorination will be carried out, or prepared in a separate reaction vessel and injected into the fluid bed of a fluorinator. It is necessary that the U₃O₅ be fluorinated during its residence time in the fluid-bed medium, in order to minimize elutriation of the U₃O₅ powder to cooler portions of the reactor, where residence with U₃O₅ powder to other to obtain information from which the residence time necessary to completely react a particle of U₃O₅ with fluoring in a fluid bed could be calculated.

Two batches of U,Os were used in this study. The first, prepared by the New Brunswick Laboratory of the AEC and designated as NB-15 had a certified purity of 99.9+ percent. The second batch, prepared by Unione Carbide Nuclear Corporation and designated as UCN, had a uranium content of 84.99 percent (theoretical for U,Os, 84.80). The surface areas, as measured by nitrogen adsorption of the NB-15 and UCN source inatorials were 0.14 and 0.28 sq m/g, respectively. The fluorine used was commercial grade from which hydrogen fluoride was removed by passing the gas through a trap filled with sodium fluoride heated to 100 C.

The fluorination experiments were performed with a thermobalance that was specially designed for use with fluorine. One main components of this thermobalance, which has been described in detail by Johnson and Fischer, (7) are a Sartorius Seiecta analytical balance, equipped for automatic weight recording, and a vertical, tubular reaction chamber. A model sample man, upon which the U,O, powder was placed, was suspended in the reaction chamber by a Monel chain attached to the stirrup of the Sartorius balance. Fluorine was passed through a preheater before the gas entered the reactor. The flow rate of the fluorine was measured by a thermal flowmeter. A thermocouple positioned directly beneath the sample pan sensed with a Rubicon Type B potentionneter. A multipoint recording potentioned eter was used to monitor the temperature of the furnace used for pheneater as the gas, the temperature of the reaction furnace used for pheneater thermal flowmeter.

In a typical experiment, 400 mg of U₁O₂ were placed on a tated nickel pan and then lowered into the reaction chamber which was prohested to the desired temperature. During this stage of the experiment, a flow of nitrogen was maintainted through the reactor. The weight of the oxide sample was checked on the Sartorius balance while temperature equilibrium between gas

and solid was being attained. When the reaction system had reached a uniform temperature, the flow of nitrogen was stopped and a flow of fluorine at a rate of 150 cc/min was started. The weight change of the oxide sample versus reaction time was continuously recorded during the reaction period.

The data obtained in these experiments were correlated by use of the diminishing-sphere model. This treatment of the data has been discussed in detail by Johnson. (7) Briefly, in the model it is assumed that in the gassolid reaction, the solid reactant consists of spherical particles of uniform diameter, and that the reaction occurs uniformly on all the particles simultaneously, when the layer of solid is thin enough to allow saturation with the reactant gas. The reaction rate is then a function of the surface area of the particle. A mathematical treatment was developed for this kinetic model based on a gas-solid reaction occurring at a continuously diminishing spherical interface. In the final expression, the reaction rate is related to the fraction of unreacted solid as shown in the following equation:

$$(1-F)^{1/3} = 1 - k't$$
 , (1)

in which

F = the fraction of solid reacted;

 $\mathbf{k'} = \mathbf{k/r_0} \rho$, where $\mathbf{r_0}$ is the initial radius of a particle, and ρ is the bulk density;

t = reaction time in minutes.

A plot of the function $(1-F)^{1/3}$ versus t results in a straight line and the reaction rate constant can be obtained from the slope of the line.

Seven fluorination experiments with the UCN oxide and fourteen with the NB-15 oxide were performed in the temperature range from 300 to 400 C. The fluorinations required 2 hr or more at 300 C and about 20 min at 400 C. Plots of $(1-F)^{1/3}$ versus time for each of the experiments resulted in straight lines over significant portions of the data. A plot for a typical experiment is shown in Figure 5. Deviation from the expected kinetics at the beginning of the experiment was due to dilution of the fluorine by the nitrogen initially present in the reactor. The deviation at the end of the reaction period was probably due to the small quantity of solid remaining. X-ray diffraction analyses of the residues indicated that uranyl fluoride is an intermediate in this reaction.

and solid was being attained. When the reaction system had reached a note form temperature, the flow of nitrogen was stopped and a flow of finewing at a rate of 150 cc/min was started. The weight change of the oxide sample versus reaction time was continuously recorded during the reaction period;

The data obtained in these experiments were correlated by use of the diminishing sphere model. This treatment of the data has been discussed in detail by Johnson. (7) Briefly, in the model it is essemble that an ine gassolid reaction, the solid reaction occurs uniformly on all the particles of uniform diameter, and that the reaction occurs uniformly on all the particles simultaneously, when the layer of solid is thin enough to allow saturation with the reaction rate is then a function of the surface area of the particle. A mathematical treatment was developed for this atnetic model based on agas-solid reaction occurring at a continuously diminishing spherical interface. In the final expression, the reaction rate is related to the traction of unreacted solid as shown in the following equation:

17-1-592-0

Andrew ork

E = the traction of solid reacied;

k" = k'rgø, where r, is the initial radius of a particle, and our the bulk density.

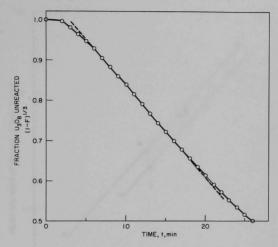
t = reaction time in minutes

A plot of the function $(1-F)^{1/2}$ versus t results in a straight line and the reaction rate constant can be obtained from the slope of the line.

Seven fluorination experiments with the UCN exide and fourteen with the NB-15 exide were performed in the temperature range from 300 to 500 C. The fluorinations required 2 hr or more at 300 C and about 20 min at 400 C. The fluorinations required 2 hr or more at 300 C and about 20 min at 400 C. The sevent in the series over significant portions of the data. A plot for a typical experiment is shown in Figure 5: Deviation from the expected kinetics at the beginning of the experiment was due to dilution at the fluorine by the nitrogen intually present in the reaction. The deviation at the end of the reaction performance analyses of the residues indicated that armyl fluoride is an intermediate in this reaction.

Figure 5 FLUORINATION OF $\rm U_3O_8$

Temperature: 401 C Fluorine Flow Rate: 120 ml/min $U_3O_8 \text{ Mesh Fraction:} -100 +325$



Rate constants were calculated from the slopes of the plots of the function $(1-F)^{1/3}$ versus time in minutes. The variation of these rate constants, k' of Equation (1), with temperature are shown in Figure 6 for experiments performed with samples of UCN and NB-15 oxides. From the slopes of the lines drawn through the two sets of data points, activation energies of 31 and 30 kcal/mole were calculated for the reactions between fluorine and NB-15 oxide and UCN oxide, respectively. The somewhat larger values of the reaction rate constants obtained with the UCN samples of U_3O_8 is probably due to the larger surface area of that material. The integrated form of the Arrhenius equation was fitted to the data to obtain the following equations representing the change in rate constant with temperature:

NB-15 oxide,
$$\log k' = -\frac{6787}{T} + 8.4438$$
 ; (2)

UCN oxide,
$$\log k' = -\frac{6599}{T} + 8.3133$$
 (3)

Temperature: 401 C Finorine Flow Rate: 130 mi/min UsO. Mosh Fronton: 108 4425



Nate constants were calculated from the slopes of the plots of the function (1-T)¹ versus 'une in minutes. The variation of these rate constants, k' of Equation (1), with temperature are shown in Figure 6 for experiments performed with samples of UCN and NB-15 oxides. From the slopes of the times dr. wa through the two sets of data points, activation emergies of 3d and 30 scal mole were calculated for the reactions between larger values of the reaction rate constants obtained with the UCN samples of U.O. is probably due to the larger satisfies are of tant material. The integrated form of the Archemius equation was fitted to the data to obtain the femperature:

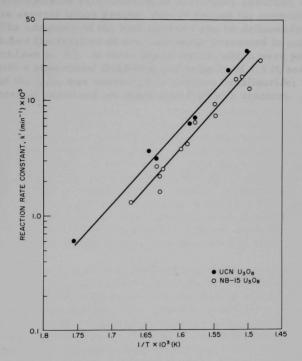
NB-18 oxider log E = Stol + 8.448 ;

UCN oxide, log k' = - 6599 + 8.3133

Figure 6

VARIATION OF RATE CONSTANT, k' (min⁻¹), WITH TEMPERATURE FOR THE FLUORINATION OF U_3O_8

Temperature Range: 300-400 CRate Equation: $(1-F)^{1/3} = 1 - k't$



By means of Equation (3), an extrapolated value of 0.6 min⁻¹ was calculated for the rate constant at 500 C, the temperature for the fluid-bed fluorination of U_3O_8 . To estimate the time necessary completely to fluorinate a particle of U_3O_8 , the kinetic equation was used in the following form:

$$1 - \frac{\mathbf{r}}{\mathbf{r}_0} = \mathbf{k}' \mathbf{t} \qquad , \tag{4}$$

in which

r = radius of the particle at time t in the fluorination; r_0 = initial radius of the particle.

Figure 6

VARIATION OF RATE CONSTANT, R. (min. 4), WITH TEMPERATURE FOR THE FLUORINATION OF U.O.

Temperature Range: 3001400 C Rate Equation: (1.7) 3 = 1 - k't



By means of Departmen (3), an extrapolaria value of 0 h tota¹² was calculated for the two constant at 500 C, the temporalitie for the fluid-bed fluorination of U₂O₂. To retinate the time necessary completely to fluorinate a particle of U₂O₂, the innetic equation was used in the following forms:

1911年春日

in which

g = radius of the particle at time t in the fluorination;
r. = initial radius of the particle.

When r is very small, that is, when the particle has been essentially completely converted to uranium hexafluoride, then the time is equal to the reciprocal of the rate constant. The solution of Equation (4) for t, with the value for the extrapolated rate at 500 C, gave a value of 1.7 min. It has been calculated (5) that the residence time of a $12-\mu$ -diameter particle in a fluid bed at a superficial gas velocity of 0.67 ft/sec would be 24 min. Therefore, if the extrapolated rate constant is reasonably accurate, a residence time which is several times greater than is needed for complete reaction is available. The adequacy of the rate constant can be deduced from the data for the fluid-bed fluorination of uranosic oxide presented in another section of this report (see p. 9). In these experiments, which were performed at 500 C and with a superficial fluidizing gas velocity of 1.5 ft/sec, more than 99 percent of the U_3O_8 was converted to uranium hexafluoride; the alumina fluid bed material contained not more than 0.05 w/o uranium.

When I is very small, that is, when the particle has been essentially completely converied to unaddum hexadiaprided then the time is equal to the reciprocal of the rate constant. The solution of Equation (4) for 1, with the value for the extrapolated rate at 500 (2, gave a value of 1.7 min. It has been calculated(5) that the residence time of a 12-µ-diameter particle in a fluid bed at a superficial gas velocity of 0.07 M/sec would be 24 min. Therefore, if the extrapolated rate constant is reasonably accurate, a residence time which is several black greater than is needed for complete reaction is available. The adequary of the rate constant can be deduced from the data for the fluid-bad duoramenton of vrances; exide presented in another section of the report (see p. 9). In these experiments, which were performed at 500 C and with a superficial fluid-ling gas velocity of 1.5 M/sec, more than 99 percent of the UyO, was converted to uranium hexalluoride; the aluminative material contained not more than 0.05 w/o uranium.

VI. SUMMARY

In the conceptual flowsheet of the fluid-bed fluoride volatility process, the uranium and plutonium contents of spent oxide fuels will be recovered by fluorination to produce the volatile hexafluorides of uranium and plutonium. Laboratory-scale work has been concerned with the fluorination of U_3O_8 in a $1\frac{1}{2}$ -in.-diameter fluid-bed fluorinator, performed to develop and test apparatus and procedures for use in future work in which plutonium will be handled. The oxide U_3O_8 was used because it would be the major product obtained in an oxidative decladding step which has been proposed for the removal of uranium and plutonium from stainless steeland Zircaloy-clad fuel elements.

In the present tests, the powdered $\rm U_3O_8$ was injected into the fluid bed by means of a fluidizing nitrogen stream. Fluorine was introduced into the fluid bed just above the point at which the powder entered the bed. Experimental investigation of the effect of parameters such as temperature, $\rm U_3O_8$ elutriation from the fluidized bed, and duration of the fluorination period upon the reaction. A scheme employing two fluorination periods at a temperature of 500 C has been developed; during the first period, $\rm U_3O_8$ is fed into the fluid bed and fluorination is carried out simultaneously with 20 v/o fluorine in the gas phase; during the second period, a gas phase containing 100 percent fluorine is recirculated through the fluid bed for a period of 5 hr. By means of this reaction scheme, more then 99 percent of the $\rm U_3O_8$ fed to the fluid-bed reactor was converted to uranium hexafluoride.

Reaction rates have been measured by means of a thermobalance for the reaction of U₃O₈ with fluorine over the temperature range from 300 to 400 C. Two samples of U₃O₈ were used; one was an analytical standard sample, the other was commercially produced material. The data have been correlated by means of a diminishing-sphere kinetic model which relates the reaction rate constant to the fraction of unreacted oxide. The reaction rate constants for the commercially produced material were slightly higher than those for the analytical standard sample at the same temperatures. An average value of 30 kcal/mole has been calculated for the activation energy of the fluorination reaction which, within experimental error, was found to be the same for the two materials tested. Equations relating the change in reaction rate constant with temperature were derived. An estimate was made of the time required completely to convert a particle of uranosic oxide having a diameter of about 10 μ to uranium hexafluoride at 500 C. The estimate, which was based on an extrapolated value of the rate constant, resulted in a value of less than 2 min.

Fuel-element mockups, which consisted of $5\frac{1}{2}$ -in.-long sections of $\frac{1}{2}$ -in.-diameter stainless steel or Zircaloy tubing packed with uranium dioxide pellets, were oxidized in a fluid bed at 450 C with air as the oxidant and fluidizing gas. Slots $(\frac{1}{8}$ in. x $\frac{1}{32}$ in.) were milled along the length of the cladding tubes at $\frac{3}{8}$ -in. intervals between the ends of the slots to promote the

In the concepted flowerest of the fluid-bed il unide volatility process, the visitium and entonium contents of apont oxide fuele will be recovered by therination to produce the volatité her alternates of uranium and platenium. Laboratory scalle work has consecued with the fluorication of V₁O₂ in a 1½-im-diameter fluid-bed decrinator, penformed to develop and test apparatus and procedures for use in value work in which platenium will be handled. The exist U.O., was used because it would be fine major product shrained in an existive neglatifies are punished has been proposed for the removal of uranium and purentum from stainless steel-and Zircziory-clad fuel elements.

In the present tests, the powdered U,C, was injected into the fluid had by means of a fluid stream. Fluorine was introduced into the fluid had by means of a fluid stream attends. Fluorine was introduced into the fluid had by the fluid had been as within the powder emerch the bed. Experimental investigation of the effect of praintings with a the fluid interpretation.

DyO, electristics from the fluidsed bedy and direction of the fluorination periods at a period upon the reaction. A accesse employing the first period, UyO, is camperature of 500 C has been developed, during the first period, UyO, is feet that had and fluorine in the gas chase, during the recond name on the first passes contained to the fluid had for a family 100 percent themselves to the recond name of the second of the strength of the UyO, ted to the fluid-had reaction was converted to maximum hazaflowides.

Rendrion rates have intermed by means of a thermobalance for the reaction of U.O. with thiorine over the respective range from 300 to sample, the other was commercially produced matched. The days have been correlated by means of a dignificantly produced matched. The days have been the reaction rate constants for the commercially produced matched. The days have been rate constants for the commercially produced matched exide. The reaction than those for the smally that standard and of the same temperatures. An average value of 30 scale mole has been calculated for the acquired energy of the fluorination reaction which which experimental from the echyptratures. An earlies are the same for the same of the same constant. The same for the same of the same of the same for the same same for the same for the same same for the same same for the sam

Fuel-element modespe, which consisted of 5 - n.-long sections of \$2.50. -diameter stainless steel or Zircaloy tubing parked with uranism dioxide policies, were oxidized in a fluid bed in \$50 () with air as the oxidized and fluidizing gas. Slots (\$\frac{1}{2}\$ in \$x_{\operation}\$ pinc.) were until equality the length of the cladding bullet at \$\frac{1}{2}\$-in, intervals between the ends of the slots to promote the

splitting of the cladding during oxidation. The time necessary to split open a section of cladding along the slit line was dependent on the thicknesses of the tubing wall. In the case of stainles steel, tubes having wall thickness of 20 and 30 mils split open along their entire lengths after 2 and 4 hr of oxidation, respectively. In the case of 30-mil-thick Zircaloy, the tubing was completely split after 6 hr of oxidation. Complete removal of the $\rm U_3O_8$ product was accomplished by means of 1-2 hr of additional oxidation.

VII. ACKNOWLEDGMENT

The authors wish to acknowledge the contribution of R. W. Kessie in the design and specification of the fluid-bed equipment used in this work.

entring of the claiming during exaction. The sime necessary to spit agent a section of elading dung file shi line was deposited as the thicknesse of the tuning wall. In the case of standing steel, more having wall thicknesse to 20 and 20 miles ages along their entire lengths after 2 and 4 in all old 20 and 20 miles ages along the case of 10 milestance are specified. In the case of 10 milestance are specified to be a set of an all chief and the case of the product was recomplished to means of 12 hr of additional exidation.

THE ACTOMORAL STREET

The authors wish to alknowledge the contribution of R. W. Kegete in the dealer deal in this work

VIII. BIBLIOGRAPHY

- 1. Jonke, A. A., Fischer, J., and Mecham, W. J., Fluoride Volatility
 Processing of Low-enriched Fuels, Trans. Am. Nucl. Soc. 4, (1961).
- Jarry, R. L., et al., <u>Laboratory Investigations in Support of Fluid-bed Fluoride Volatility Process</u>. I. The Fluorination of UO₂-PuO₂ Solid <u>Solutions</u>, ANL-6742 (1963).
- 3. Loeding, J. W., et al., The Fluid-bed Calcination of Radioactive Wastes, ANL-6322.
- Kessie, R. W., <u>The Design and Construction of Thermal Flowmeters</u>, ANL-6531.
- Gabor, J., Chemical Engineering Division, Argonne National Laboratory, private communication.
- Guon, J., et al., Low Decontamination Reprocessing Studies on Irradiated UO₂ Reactor Fuel, NAA-SR-6136 (Dec 15, 1961).
- 7. Johnson, C., and Fischer, J., Kinetics of the Reaction of Sulfur Tetra-fluoride with Uranium Trioxide and Uranyl Fluoride, J. Phys. Chem., 65, 1849 (1961).

VIII BIBLIOGRAPHY

- Jorden A. Al, Fischer, J., and Mecham, W. J., Fluoride Voladility
 Processing of Low-enriched Fuels, Trans. Am. Nucl. Soc. 3, (1991).
- larry, R. L., et al., Laboratory Investigations in Support of Fluid-bed Finerade Volentity Process 1. The Fluorination of UO, PaO, Sould Solutions, AM, AMS, 1967.
- Loeding, J. W. , et at . The Fluid-bed Calcination of Radioacure Waster, ANL-6322
 - Resale, R. W., The Besign and Constitution of Thermal Flowmeters,
- Gaber, J., Chemical Engineering Division, Argenne National Laboratory, private communication.
- Gron, J., et al., Low Decontamination Reprocessing Studies on trradiated UO, Reactor Fuelt NAA-SR-6156 (Dec 15, 1981).
 - Johnson, C.; and Pischer, I., Kinetics of the Reaction of Sulfur Terrafluoride with Urantum Trioxide and Uranyi Fluoride, A. Phys. Chem., 55, 1849 (1961).

